Secondary Organic Aerosol Formation from Reaction of Isoprene with NO_3 Radicals

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Introduction

Isoprene is the most abundant non-methane hydrocarbon in the atmosphere, with emissions estimated to be ~ 500 Tg/year [Guenther et al., 1995]. Though historically, isoprene has not been considered an important precursor for secondary organic aerosol (SOA) in the ambient atmosphere, recent research -- involving both chemical analysis of ambient SOA [Limbeck et al al 2003; Claeys et al., 2004] and chamber studies of isoprene photooxidation [Kroll et al., 2005; Kroll et al., 2006] -- suggest that isoprene is in fact significant in this regard. Based on the chamber studies, a recent modeling study estimates the global SOA production rate from isoprene photooxidation to be ~ 13 Tg/yr, or ~50% of total global SOA production [Henze et al., 2007].

In this work, we investigate SOA formation from the nighttime chemistry of isoprene, specifically the oxidation of isoprene by NO_3 radicals. Field measurements have noted that isoprene mixing ratios peak before sunset, but drop rapidly after sunset, suggesting that NO_3 plays a significant role in its decay [Curran et al., 1998; Starn et al., 1998; Stroud et al., 2002; Steinbacher et al., 2005]. The rate constant for isoprene-NO_3 reactions is ~ 7 x 10^{-13} cm^3 molecule^{-1} s^{-1} at 298K [Berndt and Boge, 1997; Suh et al., 2001].

In addition to assessing the SOA production from isoprene oxidation by NO_3, we also utilize a suite of particle- and gas-phase analytical techniques to examine the chemical composition of the SOA and propose mechanisms for its formation.

Experiment Description

Caltech dual 28m^3 teflon chambers, T=21 deg C, RH <10%

Seed added: 0.015 M NH_4SO_4

Typically, isoprene is added after the seed, followed by a single pulse of excess N_2O_5. Thermal decomposition of N_2O_5 into NO_2 and NO_3 serves as the source of NO_3 radicals.

In some experiments, we use a different experimental protocol: 1) adding staggered, small pulses of N_2O_5 to isoprene, 2) slowly adding a dilute stream of N_2O_5 to isoprene, or 3) adding N_2O_5 to the chamber first, then slowly adding a dilute stream of isoprene. These variations allow us to examine more thoroughly the mechanism of SOA formation.

N_2O_5 is synthesized by mixing pure NO with ~ 2% O_3, then trapping in an acetone-dry ice bath. Between experiments, it is stored in liquid nitrogen. For injections into the chamber, a known amount of N_2O_5 is vaporized into a 500 ml glass bulb, and zero air is flowed through the bulb into the chamber.

Instrumentation

-- Gas Chromatograph (GC-FID, Agilent): isoprene mixing ratio

-- Differential Mobility Analyzer (DMA, TSI Corp): aerosol size distribution and particle number concentration

-- Chemical Ionization Mass Spectrometer (CIMS, custom modified Varian): gas-phase constituents, particularly nitroxy- and hydroxy- carbonyls, peroxides

-- Filter samples analyzed offline with iodometric colorimetry and ultra performance liquid chromatography system coupled to a time of flight mass spectrometer operated in negative mode with electrospray ionization (UPLC/(-)ESI-TOFMS, Waters): aerosol-phase peroxide content and chemical speciation

-- Quadrupole Aerosol Mass Spectrometer (Q-AMS, Aerodyne): aerosol mass distribution, chemical composition, and density

-- Particle into Liquid Sampler (PILS, Brechtel Manufacturing): aerosol-phase water-soluble ions

SOA Yield and Implications
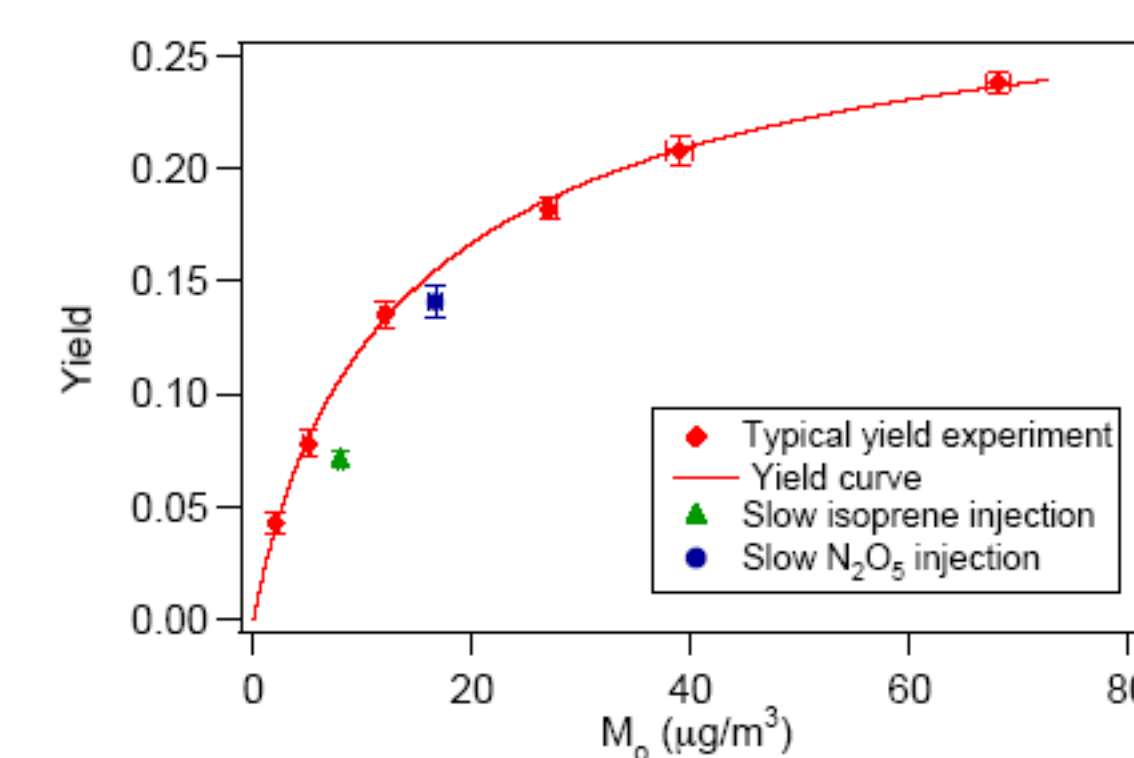
Yield curve for isoprene-NO_3 reaction, with yields from slow isoprene and slow N_2O_5 injection experiments also shown.

SOA yield (mass of aerosol formed divided by mass of hydrocarbon reacted) is well described by the semi-empirical model based on the absorptive gas-particle partitioning of two semivolatile reaction products [Odum et al., 1996]:

$$Y = \Delta M_o \left[\frac{\alpha_1 K_{om,1}}{1 + K_{om,1} M_o} + \frac{\alpha_2 K_{om,2}}{1 + K_{om,2} M_o} \right]$$

α_1 = .089, $K_{om,1}$ = .182 m^3 mg^{-1}
α_2 = .203, $K_{om,2}$ = .046 m^3 mg^{-1}

where M_o = total organic (absorbing) aerosol mass
α_i = mass stoichiometric coefficient of condensable product i
K_i = partitioning equilibrium constant for condensable product i

These yields incorporate an aerosol density estimate of 1.42 g/cm^3 obtained by comparing DMA volume distributions and Q-AMS mass distributions.

For each "typical" yield experiment, inorganic aerosol nitrate measured by the PILS, ranging from 1.6 - 2.6 $\mu g/m^3$, is subtracted from the derived aerosol mass to obtain ΔM_o. For the slow isoprene and N_2O_5 injection experiments, a comparable inorganic nitrate concentration is assumed. This nitrate is likely due to nitric acid which partitions or is reactively uptaken by the aerosol. Nitric acid is an impurity in the N_2O_5 (~10% by FTIR analysis), and can also be formed from hydrolysis of N_2O_5 with trace water in the chamber.

While the SOA yield for the slow N_2O_5 injection experiment is comparable to that of a typical experiment, the yield for the slow isoprene experiment is significantly lower. This highlights the importance of the gas-phase mechanism for SOA formation, which is discussed below.

To estimate, roughly, the contributions of isoprene-NO_3 reactions to global SOA production, we first estimate the loss of isoprene from NO_3 with the global chemical transport model GEOS-Chem (v.7-04-11), then apply an approximate, uniform SOA yield of 10% for these reactions (corresponding to M_o ~ 10 $\mu g/m^3$).

|	Emission Model	
	GEIA[a]	MEGAN[b]
Isoprene emission (Tg/y)	507	389
Global isoprene burden (Tg)	1.7	1.7
Isoprene lifetime (days)	1.2	1.6
Isoprene reacted (Tg/y) by		
Isoprene + OH	407	304
Isoprene + O_3	69	62
Isoprene + NO_3	29	21

Estimates of global isoprene production and loss from GEOS-Chem. Two different emission models, GEIA [Guenther et al., 1995; Bey et al., 2001] and MEGAN [Guenther et al., 2006], are used.

Assuming a 10% SOA yield for isoprene-NO_3 reactions, we estimate the global SOA production rate of ~ 2-3 Tg/yr. This is ~ 10% of the global SOA production estimated by Henze et al. (2007), and is comparable to the production from biogenic alcohols, sesquiterpenes, and aromatics.

Hydrocarbon	Emission (Tg/yr)	SOA Production (Tg/yr)	Burden (Tg)
terpenes	121	8.2	0.21
alcohols	38.3	1.5	0.03
sesquiterpenes	14.8	2.0	0.03
isoprene	461	13.2	0.43
aromatics	18.8	1.5	0.08
total	654	28.4	0.78

Estimated contributions to global SOA production from gas phase precursors [Henze et al., 2007]. This table does not include isoprene oxidation by NO_3.

This is a crude estimate. Gas-particle partitioning depends on total organic aerosol mass, so including an additional aerosol formation pathway will affect the yields of all other pathways in models. Also, in the ambient atmosphere, SOA yield from isoprene-NO_3 reactions will be highly dependent upon local chemistry. This is apparent when we analyze the aerosol yield data in concert with the gas- and particle-phase chemical composition data from the CIMS and filter samples, respectively; such an analysis, described below, gives us insight into key steps in the mechanism for SOA formation.

SOA formation mechanism and chemical composition
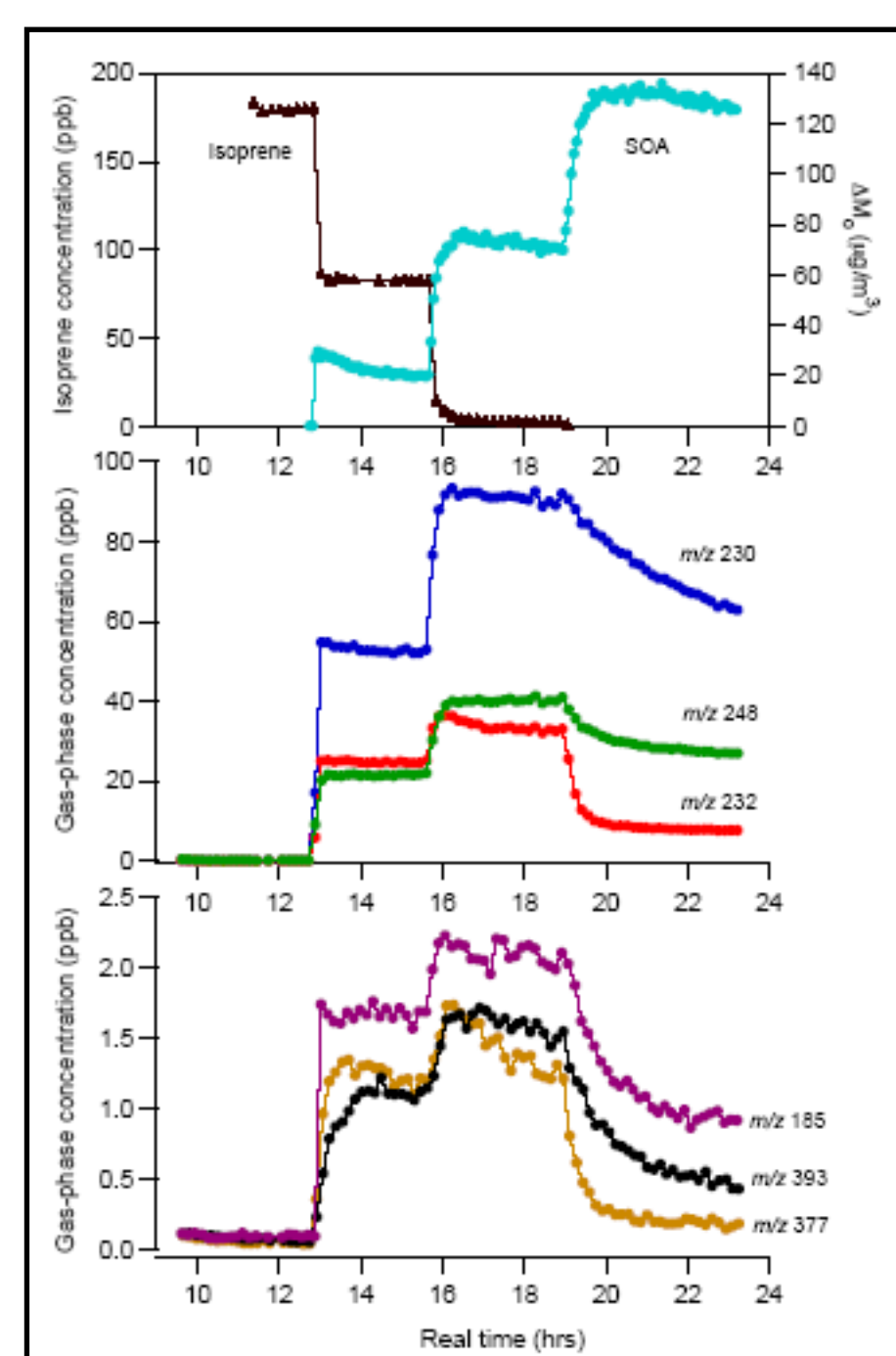
Isoprene, SOA mass, and CIMS gas phase time profiles for experiment with 3 N_2O_5 additions: ~ 120 ppb (13.0 hrs), ~ 50 ppb (15.6 hrs), and ~ 210 ppb (19.0 hours). Gas-phase concentrations are estimates based on a nominal sensitivity for the CIMS; calculating more accurate sensitivities is the focus of ongoing work.

The experiment with staggered pulses of N_2O_5 provides insights into the major precursors to aerosol growth.

The CIMS ionizes analytes via clustering with CF$_3$O$^-$ [Crounse et al., 2006], forming detected ions at m/z MW + 85. The major first generation products appear at m/z 230, 232, and 248, corresponding to MW 165, 167, and 183, respectively. These are the C5-nitroxycarbonyl, C5-hydroxynitrate, and C5-nitroxyhydroperoxide that result from the nitroxyperoxy radical formed from the initial NO_3 addition to isoprene [Jay and Stieglitz, 1989; Skov et al., 1992; Kwok et al., 1996; Berndt and Boge, 1997].

After the first two pulses, the isoprene is reacted completely, so the third pulse of NO_3 exclusively reacts with the first generation products (which still have a double bond). We note that the decay of m/z 232 is highly correlated with aerosol growth, indicating that it may be an important precursor to SOA formation.

We also see three other compounds, which, while less abundant, also have time traces consistent with compounds contributing to SOA formation: m/z 185, 377, and 393 (MW 100, 292, and 308, respectively). The latter two compounds indicate the formation of C10 compounds from RO$_2$-RO$_2$ self- and cross- reactions.

The formation of ROOR compounds, if generalizable to the ambient atmosphere, may be a significant process for SOA formation, as it represents an efficient pathway for creating low vapor pressure compounds.
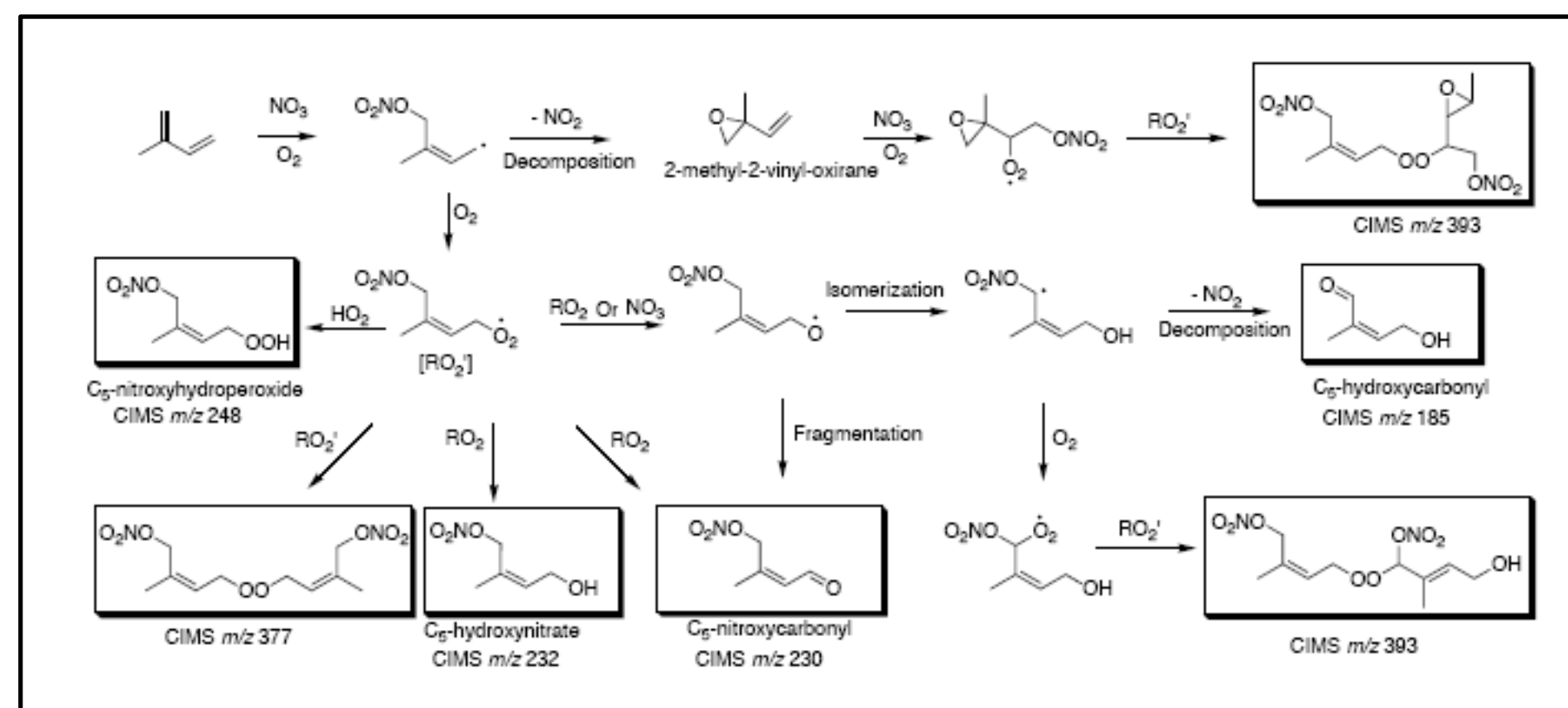
Proposed mechanisms for the formation of important gas-phase intermediates observed by the CIMS. Multiple structural isomers are likely. R'O$_2$ refers to the original isoprene nitroxyperoxy radical, while RO$_2$ refers to a generic peroxy radical.

The high resolution mass measurements of aerosol components detected by UPLC/(-)ESI-TOFMS allow for generally unambiguous identification of molecular formulae. The aerosol-phase composition derived from these formulae can be linked to the gas-phase data to validate the important gas-phase SOA precursors and establish mechanisms for SOA formation, e.g., for CIMS m/z 393:
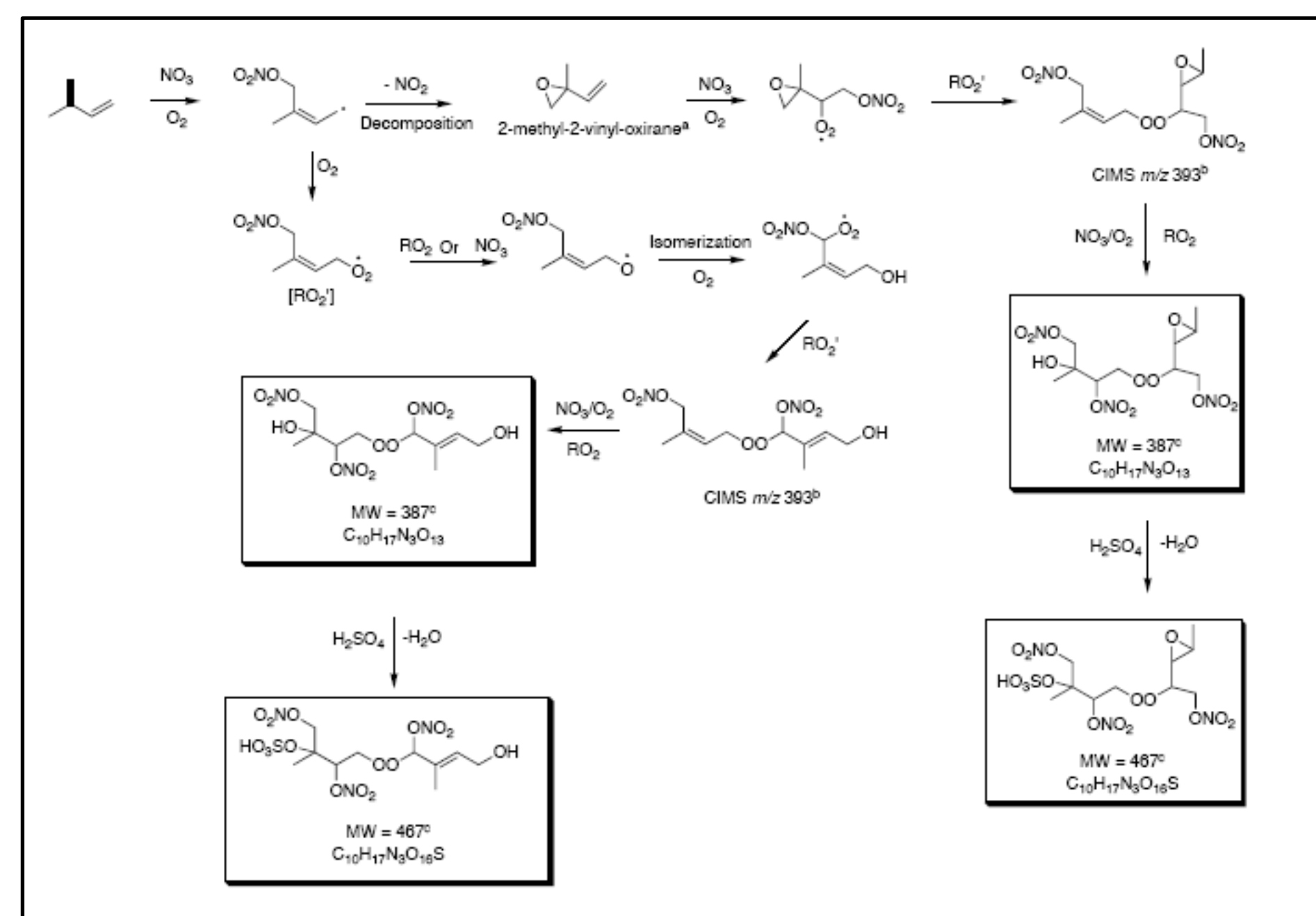

Proposed SOA formation pathways from MW 308 C10 peroxide (CIMS m/z 393). Oxidations may possibly occur both in the gas phase and heterogeneously. The molecular formulae of all boxed compounds were identified by UPLC/(-)ESI-TOFMS, though the structures presented here are proposed, and have yet to be definitively deduced. The MW 467 sulfate was only detected in seeded experiments.

The offline iodometric colorimetry measurements (not shown) confirm that a significant fraction of the SOA mass consists of organic peroxides (~ 30%), further supporting our proposed mechanisms.

Importance of RO$_2$-RO$_2$ reactions

For the slow isoprene and slow N_2O_5 addition experiments, the same amount of isoprene (~ 40 ppb) is consumed, but the SOA yield is about two times higher for the slow N_2O_5 addition.

This highlights the importance of RO$_2$-RO$_2$ reactions to SOA yield. Most of the important SOA precursors (i.e., CIMS m/z 232, 377, and 393), result exclusively from RO$_2$-RO$_2$ reactions, which are favored by the slow N_2O_5 addition. The "hook" for the growth curve in this case shows significant SOA growth occuring from the oxidation of second (or higher) generation products, further establishing the importance of these gas phase intermediates.
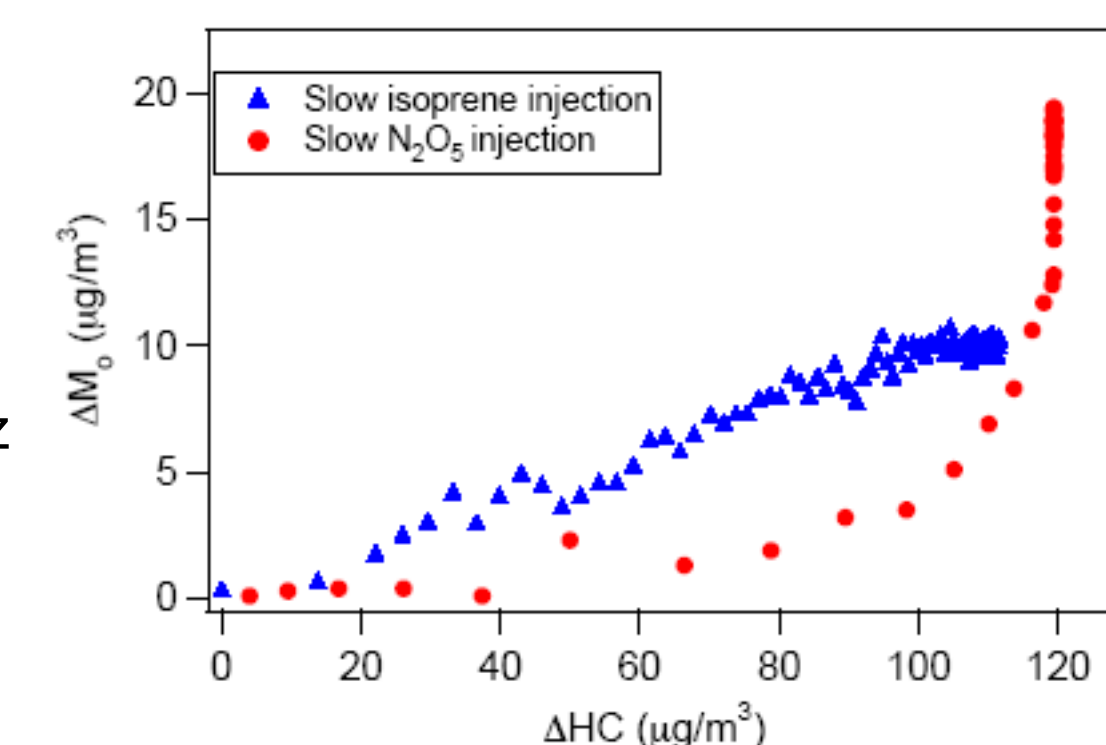
Growth curves (aerosol mass as a function of hydrocarbon reacted) for slow isoprene injection (RO$_2$-NO$_3$ reactions favored) and slow N_2O_5 injection (RO$_2$-RO$_2$ reactions favored)

The slow isoprene addition, however, favors RO$_2$-NO$_3$ reactions. Fewer SOA precursors are produced in this case, though those that do form are quickly oxidized to aerosol by excess NO$_3$. Thus, aerosol growth is initially faster, but ultimately not as large, and we cannot distinguish between first and higher generation contributions to the growth.

Both the Q-AMS and filter sample analyses (not shown) indicate that the SOA formed in each case is chemically similar, so the differences in growth are not due to the two cases having different SOA formation pathways. Instead, the differences arise because those pathways (mostly RO$_2$-RO$_2$ reactions) are more favored for the slow N_2O_5 addition compared to the slow isoprene addition.

Therefore, the extent to which our experimental SOA yields are applicable to the real atmosphere will depend on the competition between RO$_2$ and NO$_3$ radicals -- as well as HO$_2$. More laboratory and field studies are needed to assess the balance of these reactions in the ambient atmosphere.

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